PREPARATION AND CHARACTERIZATION OF ALUMINA LOADED TITANIA IN THE PHOTOREDUCTION OF CO_2

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ABSTRACT

Nowadays, the atmospheric concentration of carbon dioxide (CO_2) had been increased due to the globalization and technology created by human activities. CO_2 is one of the major contributors to greenhouse effects which will leads to global warming. Therefore alternative routes should be taken to overcome this problem. One of the best remediation is to transform CO_2 into useful hydrocarbon by using photoreduction. Photoreduction is one of the methods which can be used to reduce the concentration of CO_2 released to the atmosphere. The aim of this study was to find a new catalyst produced with the best method in photoreduction process. Catalyst plays an important role to accomplish specific tasks with greater efficiency and speed. The metal oxides, Alumina (Al_2O_3) was chosen to be use in this research which was loaded with Titania (TiO_2). Al_2O_3-TiO_2 catalyst was prepared by using two different methods which are sol gel and hydrothermal method. The prepared catalysts were analyzed and characterized by using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) method. Experimental results demonstrated that hydrothermal method was a promising technique for preparing Al_2O_3-TiO_2 photocatalysts as it fulfilled the requirement properties to enhance the photocatalytic activity of TiO_2 in the photoreduction process. Based on SEM analysis, the surface morphology of Al_2O_3-TiO_2 catalyst exhibits well arranged aggregates with many small spherical particles. Meanwhile FTIR analysis, the presence of Al-O bonds in the TiO_2 powder was successfully obtained as the peaks of 947.75 cm^{-1} fall in the general range of Al-O vibrations. Other than that, based on XRD pattern of Al_2O_3-TiO_2 it revealed the existence of polymorphs anatase TiO_2 which usually shows greatly superior in photoactivity of TiO_2. Most importantly, based on BET analysis, the prepared Al_2O_3-TiO_2 catalysts show a great crystal growth with 153.8599 m^2/g specific surface area and 8.8 nm of pore size diameter. A nano size material leads to improvement in the electron hole pair separation and enhance the photoactivity of TiO_2.

ABSTRAK

Pada masa kini, jumlah kepekatan karbon dioksida (CO_2) di dalam udara telah meningkat disebabkan oleh globalisasi dan teknologi yang dicipta oleh aktiviti manusia. CO_2 adalah salah satu penyumbang utama kepada kesan rumah hijau yang akan membawa kepada pemanasan global. Oleh itu, langkah alternatif harus diambil untuk mengatasi masalah tersebut. Salah satu kaedah yang terbaik untuk menjadikan CO_2 kepada jenis hidrokarbon yang berguna dengan menggunakan kaedah photoreduksi. Photoreduksi adalah salah satu kaedah yang boleh digunakan untuk mengurangkan kadar kepekatan CO_2 yang dilepaskan ke atmosfera. Tujuan kajian ini adalah untuk mencari mangkin baru yang akan dihasilkan dengan kaedah yang terbaik dalam proses photoreduksi. Mangkin memainkan peranan yang penting untuk menyempurnakan tugas-tugas tertentu dengan lebih berkesan dan pantas. Oksida logam, Alumina (Al_2O_3) telah dipilih untuk digunakan dalam penyelidikan ini yang akan dicampur dengan Titania (TiO_2). Mangkin Al_2O_3-TiO_2 telah disediakan dengan menggunakan dua kaedah yang berbeza iaitu kaedah sol gel dan kaedah hidroterma. Mangkin yang telah disediakan, dianalisa dan dicirikan dengan menggunakan Mikroskop Elektron Imbasan (SEM), Spektroskopi Fourier Transform Infrared (FTIR), pembelauan X-Ray (XRD) dan kaedah Brunauer-Emmett-Tellar (BET). Keputusan uji kaji menunjukkan bahawa kaedah hidroterma adalah satu teknik yang bagus untuk menyediakan mangkin Al_2O_3-TiO_2 kerana ia memenuhi ciri-ciri untuk meningkatkan kadar aktiviti photobermangkina TiO_2 dalam proses photoreduksi. Berdasarkan analisis SEM, morfologi permukaan mangkin Al_2O_3-TiO_2 mempamerkan agregat yang disusun dengan banyak zarah sfera kecil. Sementara itu, analisa FTIR, membuktikan bahawa kehadiran ikatan Al-O dalam mangkin TiO_2 telah berjaya diperolehi iaitu pada puncak 947.75 cm^{-1} yang jatuh dalam julat am getaran ikatan Al-O. Selain daripada itu, berdasarkan corak XRD Al_2O_3-TiO_2, ia mendedahkan kewujudan fasa anatase zarah TiO_2 yang biasanya menunjukkan banyak manfaat dalam photoaktiviti TiO_2. Paling penting, berdasarkan analisa BET, mangkin Al_2O_3-TiO_2 yang

disediakan menunjukkan pertumbuhan kristal yang hebat yang mempunyai 153.8599 m^2 / g permukaan kawasan tertentu dan saiz diameter liang zarah sebanyak 8.8 nm. Bahan saiz nano membawa kepada peningkatan dalam lubang pemisahan pasangan elektron dan akan meningkatkan kadar photoaktiviti TiO_2.

CHAPTER 1

INTRODUCTION

1.1 Background study

Carbon dioxide (CO_2) is one of the green house gases which cause the global warming. According to International Energy Agency (IEA) (2011), the atmospheric concentration of CO_2 has recently increased about 280 parts per million in volume (ppmv) due to the globalization and technology created by human activities.

Some impacts of the increased of CO_2 emissions concentrations may be slow to become apparent since stability is an inherent characteristic of the interacting climate, ecological and socio-economic systems. Besides that, even after stabilisation of the atmospheric concentration of CO_2, anthropogenic warming and sea level rise are still would continue for centuries due to the time scales associated with climate processes and feedbacks (IPCC, 2007). Some changes in the climate system would be irreversible in the course of a human lifespan.

Moreover, due to the long lifetime of CO_2 in the atmosphere, stabilising concentrations of greenhouse gases at any level would require large reductions of global CO_2 emissions from current levels. The lower the chosen level for stabilisation, the sooner the decline in global CO_2 emissions would need to begin, or the deeper the emission reduction would need to be on the longer term (IEA, 2011).

Table 1.1 shows the world CO_2 emissions from fossil fuel combustion in 2006 and 2008, with IEA projection for 2020. From Table 1.1, IEA had predicted that the amount of CO_2 emissions will increase by year.

Table 1.1: World CO_2 emissions from fossil fuel combustion in 2006 and 2008, with IEA projection for 2020

Emissions	Growth Rate, 2006-2015	Growth Rate, 2015-2020	CO_2 Emissions, 2006	CO_2 Emissions, 2008	CO_2 Emissions, 2020
By Fuel:	Percent		Million Tons Carbon		
Coal	3.1	1.6	3,185	3,431	4,555
Oil	1.3	0.9	2,937	2,947	3,454
Gas	2.0	1.5	1,484	1,602	1,918
By Sector:					
Power Generation	2.9	1.6	3,119	3,250	4,365
Coal	3.2	1.7	2,273	2,365	3,300
Oil	-0.4	-1.9	241	236	211
Gas	2.8	2.0	605	650	853
Total Final Consumption	1.7	1.1	4,123	4,323	5,090
Coal	2.7	1.1	855	990	1,150
Oil:	1.5	1.2	2,515	2,527	3,033
(i) of which transport	1.7	1.3	1,708	1,746	2,126
(ii) of which marine bunkers	1.0	1.0	159	158	326
(iii) of which international aviation	2.2	1.8	108	124	145
Gas	1.4	1.2	754	807	907
Other Energy Sector			364	406	472
Total CO_2 Emissions	2.2	1.4	7,606	7,980	9,927

Source: IEA (2010)

A strategic plan had been suggested to prevent the environmental and economic collapse as shown in Table 1.2 (Rattan, 2004). Unfortunately, the remediation of CO_2 can be physically stored or chemically transformed, but these methods only overcome the problem temporarily. Thus, CO_2 must be transform into another useful or non-toxic compound in order to solve these problems permanently (Hsiang et al., 2002).

Table 1.2: CO_2 Emissions Reductions and Sequestration in 2020 (Rattan, 2004).

Action	**Amount**
Energy Restructuring	Million Tons of Carbon
Replacing fossil fuels with renewables for electricity and heat	3,210
Restructuring the transport system	1,400
Reducing coal and oil use in industry	100
Biological Carbon Sequestration	
Ending net deforestation	1,500
Planting trees to sequester carbon	860
Managing soils to sequester carbon	600
Total Carbon Dioxide Reductions in 2020	**7,670**
Carbon Dioxide Emissions in 2006	9,350
Percent Reduction from 2006 Baseline	**82.0**

Source: Rattan (2004)

Fujishima and Honda (1972), had discovered the photocatalytic splitting of water on titania (TiO_2) semiconductor electrode. Due to the new discovery of the usage of semiconductor, the researchers pay more attention towards it as a medium in photocatalysis activity for environmental protection (Hsiang et al., 2002). Photocatalysis is a catalytic process that occurs on the surface of semiconductor materials under the irradiation of photons (Fujishima and Honda, 1972). Yamashita et al., (1998) identified that photocatalysis has been exploited for various environmental process such as deodorization, water purification, air purification, sterilization and soil proof. In addition, Yamashita et al., (1998) had proven that CO_2 has been reduced

efficiently with water by photocatalysis. Thus, the photoreduction process is suitable to be use to reduce the concentration of CO_2.

Photoreduction is one of the methods which can be used to reduce the concentration of CO_2 gas and convert it to become non-toxic and reusable hydrocarbon resources. In this process, the solar energy had been use as an energy input because it can be supplied naturally and due to its abundant (Wu and Chih-Yang, 2001). Photoreduction by using TiO_2 photocatalyst is being widely studied as a relatively new technique of pollution abatement. TiO_2 is a commonly used photocatalyst because of its stability in an ultraviolet (UV) light and water (Wan-Jian et al., 2010). However, the need of UV excitation source restricts its technological utility for limited applications. For widespread applications, TiO_2 photocatalyst effective in solar light or light from visible region of the solar spectrum need to be developed as future generation photocatalytic material. TiO_2 absorbs only 5 % energy of the solar spectrum hence numerous studies have been performed to extend the photoresponse and photocatalytic activity by modifying its crystal growth, doping and heterostructuring design of high-efficiency semiconductor photocatalysts which have substantial influences on light-response range, redox potentials of photoinduced charge carriers, and bulk and surface separation probability of the photocatalysts (Gang et al., 2009).

Significantly, the crystal growth is a key parameter in controlling the phase, shape, size, crystallinity and surface area of TiO_2 photocatalysts. Soria et al., (2003) claimed that the surface of TiO_2 photocatalysts have a substantial influence on modifying electronic structure and the construction of heteroatomic surface structures modification by doping with organic polymers, metal and non-metal ions has been proven to be an efficient route to improve the photo-catalytic activity of TiO_2 under solar light irradiation (Gang et al., 2009). Many researchers have paid attention in developing modified TiO_2 powder catalyst but using the powder catalyst has the disadvantages like stirring during the reaction and separation of catalyst after each run (Zhang et al., 2003).

According to Lee et al., (2005), metal oxide has attracted increasing attention due to its effectiveness in realizing visible-light photocatalytic activity of wide bandgap

semiconductor photocatalysts. Besides that, according to Gang et al., (2009), the other key factors in adjusting the spectral distribution of the induced electronic states of those dopants and reconstructing favorable surface structure of the photocatalysis is the chemical states and locations of dopants. Heterogeneous or heterostructures of TiO_2 photocatalysts seem to possess advantages in more efficiently utilizing solar light by combining different electronic structures than a single phase semiconductor photocatalysts (Gang et al., 2009). The interrelationship among the key factors in crystal growth, doping and heterostructuring of TiO_2 semiconductors for photocatalysis is illustrated schematically in Figure 1.1.

Figure 1.1: Correlation of key factors in crystal growth, doping and heterostructuring of semiconductors for photocatalysis. (CB: conduction band; VB: valence band)

Source: Gang et al., (2009)

Furthermore, the movement electron and hole from one component unit to another with appropriate band edge positions can significantly decrease the electron-hole recombination probability and increase the lifetime of charge carriers, thus enhanced the efficiency of the photocatalytic activity (Paola et al., 2004). Therefore, it will increase the photoactivity of TiO_2. In this research, Aluminium Oxide (Al_2O_3) was

used as the source of metal oxide loaded on TiO_2 by using two methods which are sol gel method and hydrothermal method.

1.2 Problem statements

Carbon dioxide (CO_2) is a major source of the greenhouse gas effect which causes the increasing in the Earth's temperature. The concentration of atmospheric CO_2 has increased by about 35 % since the beginning of the age of industrialization. This is due to the globalization and human activities such as the combustion of fossil fuels and deforestation. In order to solve this matter, the researchers work hard to find the best remediation for this problem. One of the best method uses is to develop a heterogeneous catalyst.

The aim of this study is to prepare and characterize the metal oxide loaded Titania (heterogeneous catalyst) by using two different methods which are the sol gel method and hydrothermal method in order to enhance the properties of Titania so that the photocatalytic activity in photoreduction process can be increase.

1.3 Research Objectives

The main objectives of this study are to:

a) Prepare Al_2O_3-TiO_2 as a catalyst to be used in photoreduction process.
b) Characterize the prepared Al_2O_3-TiO_2 and pure TiO_2 catalyst for it physical and chemical properties.

1.4 Scope of Research

This study will focus in two main areas that are;

i. To prepare a metal oxide loaded on TiO_2 and pure TiO_2 using two different methods which are sol gel method and hydrothermal method.

ii. To characterize the chemical and physical properties of the prepared catalysts by using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Brunauer-Emmett-Tellar (BET) method.

1.5 Rationale & Significance

In this study, the preparation and characterization of metal oxide loaded Titania in photoreduction process will be investigated. According to Aprile et al., (2008) several factors which affect the efficiencies of a particular metal oxide photocatalyst are including the particle size, crystal phase, purity, band gap, flatband potential, surface treatments, and co-catalysts.

Surface reactions of the heterogeneous catalyst play the important role in promoting the electron-hole pairs separation. The improvement in efficiency of catalytic activity will increase if the surface area of the catalyst is increase. In addition, Paola et al., (2004) also stated that the catalyst should have the electron hole combination and interfacial change transfer. So that the improvement in the separation photoproduced of electron hole pairs can be increased. Thus, it is significant to determine the characteristic of the catalyst so that the efficiency of the photoreduction can be achieve (Slamet et al., 2004).

Navio et al., (1999) suggested that by investigating the characteristic and the best method used in the preparation of the catalyst, the amount of CO_2 produce to our environment can be reduced by photoreduction process.

CHAPTER 2

LITERATURE REVIEW

2.1 Titania (TiO_2)

Hashimoto et al., (2004) reported that the Rossi from USA is the first successful attempt to produce relatively pure titania from ilmenite ore in 1908. TiO_2 is a type of semiconductor which had been widely used as white pigment in the plastic, paint and paper industries. The first titanium pigment company which initially produced composite pigments commenced production is at Niagara Falls in 1918. Another main landmark in the history of TiO_2 is it was develop by using improved method of thermal hydrolysis conducted by Blumenfeld in 1920 in France. The technology was licensed to a number of companies in Europe as well as in USA. The growth of the production and use of TiO_2 white pigments began in the early 1930s and continues until recently. Other than that, it is also used as a UV absorber in sunscreen. Hashimoto, et al., (2004) also claimed that TiO_2 is non-toxic semiconductor so it safe to humans and environmental.

Gao, (2002) investigated that TiO_2 has the most efficient photoactivity, the highest stability and the lowest cost which lead to the increasing use of TiO_2 as a photocatalyst for pollution reduction due to its strong oxidizing power, stable at different pH and favorable band gap energy. Paola et al., (2004), asserted that TiO_2 plays the important roles in promoting the reduction of CO_2. It is use to support the materials for metal or metal oxides due to its ability to modify the catalytic properties of the supported phase (Slamet et al., 2004).

Lusvardi et al., (1998) claimed that titanium cations are present in a variety of different coordination environment and oxidation states. The numerous surface valence states of TiO_2 are capable of interacting with adsorbed species in unique ways facilitating many different chemical reactions. Sherill et al., (2001) mentioned that surface oxygen plays an important role in the state of titanium surface atoms. Fully oxidized surfaces show traits similar to the transition metal complexes. Moreover, the fully oxidized surface has insulator properties with very low electrical conductivity. The removal of surface oxygen causes electron transfer into the 3d orbital. Therefore at non-zero temperatures, electrons can be thermally excited to conduction band creating a more conductive surface. Surface oxygen can be removed creating vacancies via several methods which are, annealing in hydrogen, annealing in vacuum (Lusvardi et al., 1998) and argon sputtering under ultrahigh vacuum conditions (Sherrill et al., 2000). This creates a useful material for catalytic and gas sensing applications (Erkan et al., 2006).

2.1.1 Crystalline structure of TiO_2

TiO_2 particles are referred as primary, aggregates or agglomerates. Primary particles are the single crystals that are bound by crystal planes. Meanwhile, aggregates are the sintered primary particles that are connected by a crystals faces. Agglomerates are multiple primary particles and aggregates that are held together by van der Waal's forces. The diameter of the particles which had been scattering by TiO_2 with the presence of light is maximized with 0.2-0.3 μm and most commercial products that are used as pigments have primary particles size within this range. Besides that, the range of ultrasonically dispersed primary particles and aggregates is narrow and generally ranges from < 0.1 to 0.5 μm (Swiler, 2005).

Supan et al., (2011) stated that TiO_2 has three kinds of different crystal structure forms which are anatase, brookite and rutile. They are all composed of octahedral groups of oxygen atoms around titanium (Ti) exhibiting the characteristic six coordination of this element. However the position in which the groups are linked together is different for each mineral (Bragg et al., 1965).

Crystalline structure of rutile as shown in Figure 2.1 has a dimension of 4.58 Å, while the c dimension is 2.95 Å with 6:3 coordination. From Figure 2.1, every Ti atom is surrounded by oxygen atoms approximately at the corners of a regular octahedron and every oxygen atom by three Ti atoms approximately at the corners of an equilateral triangle. This atomic arrangement is one of the standard types for AB_2 compounds in which the atom is in six-coordination and it is also characteristic of a very large number of crystals. The crystal form structure of rutile can be seen at Figure 2.2.

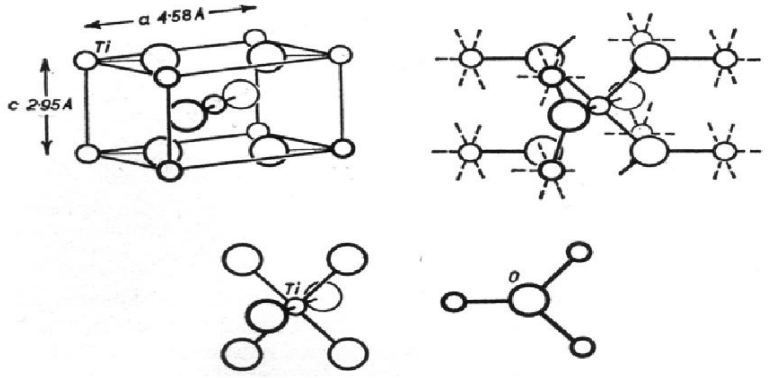

Figure 2.1: The structure of rutile. Above (left) unit cell and (right) bonds between Ti and O atom. Below environment of Ti and O atoms

Source: Alp (2009)

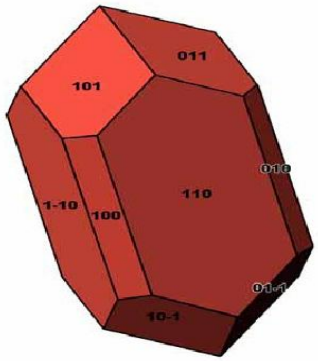

Figure 2.2: Crystal form structure of rutile

Source: Alp (2009)

For anatase, it has 3.78 Å as its dimension and 9.50 Å as it c dimension as shown in Figure 2.3. From Figure 2.3(a), it shows the position of the atoms in the body-centered unit cell. While Figure 2.3(b), shows the links between Ti and O atoms. As in rutile, shows in Figure 2.3(c), every Ti atom is between six O atoms and every O atom is between three Ti atoms. Anatase and rutile are thus alternative forms of 6:3 coordination. The crystal form structure of anatase can be seen at Figure 2.4.

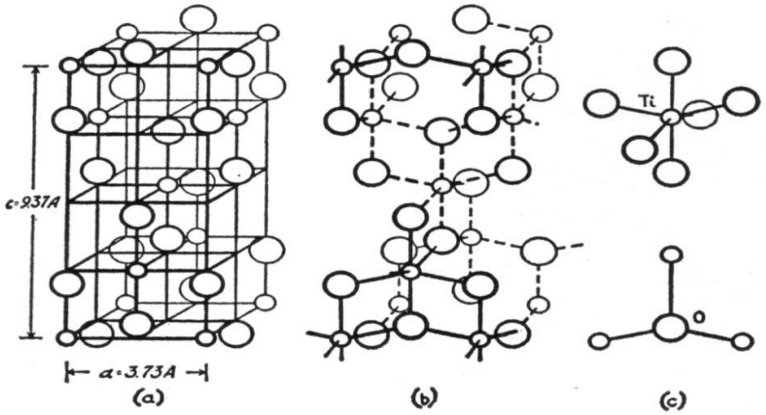

Figure 2.3: The Structure of anatase (a) Unit cell (b) bonds between Ti and O, (c) environments of Ti and O atoms which are closely similar to those in rutile

Source: Alp (2009)

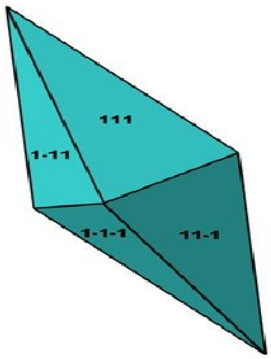

Figure 2.4: Crystal form structure of anatase

Source: Alp (2009)

Meanwhile, for brookite, it has an orthorhombic structure and its a, b, and c dimensions are 9.14 Å, 5.44 Å and 5.15 Å. The structure is shown in an idealized form in Figure 2.5 and it can be seen that the structure is quite complex compared to the other polymorphs.

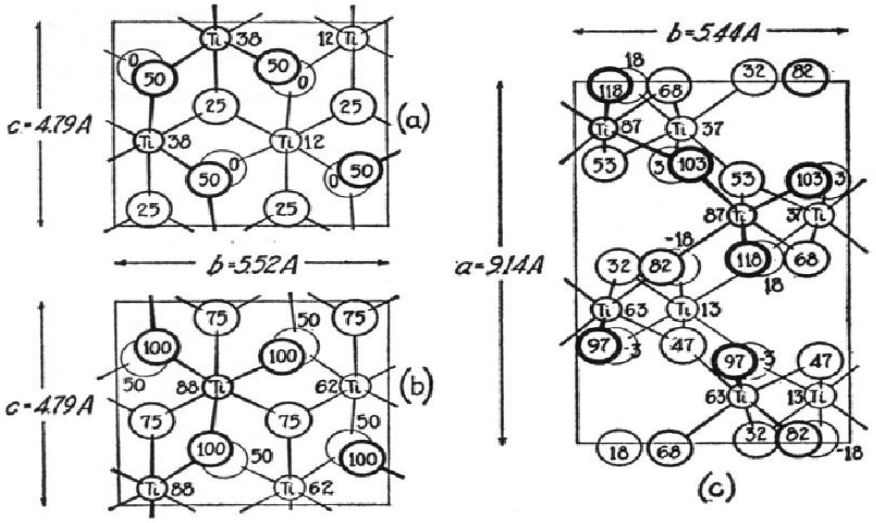

Figure 2.5: The structure of brookite in idealized form. (a) The oxygen atoms at height 50 being common to both (b) is to be superimposed on. (c) The actual structure projected on (001). Oxygen atoms which should be superimposed have been displaced symmetrically

Source: Alp (2009)

As in rutile and anatase, each Ti atom is surrounded by an octahedral group of oxygen atoms. In all three forms of TiO_2, the titanium-oxygen distance lies between 1.9 Å and 2 Å. Neighbouring oxygen atoms are between 2.5 Å and 3 Å apart, the smaller distance obtaining when the pair of oxygen atoms is linked to the same two titanium atoms. The crystal form structure of anatase can be seen at Figure 2.6.

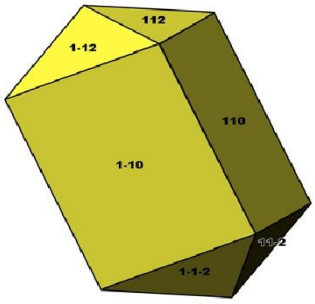

Figure 2.6: Crystal form structure of brookite

Source: Alp (2009)

Chen et al., (2003), claimed that anatase and brookite are meta-stable phases and irreversibly transform to the thermally stable rutile phase upon heat treatment in the temperature range from 450 °C to 900 °C. Better crystallinity and larger crystallite size of catalyst also can be obtained at the same time. Many studies have clarified that anatase exhibited greater photocatalytic property than rutile due to the highly hydroxylate surface responsible for photocatalytic reaction which is readily formed in the anatase structure. Anatase nanoparticles can be fabricated into various device forms for solar cell and fuel cell applications. Therefore, the stabilization of anatase phase becomes a subject of interest to be studied (Qui, 2006).

2.1.2 Capacity, Production and consumption of TiO_2

Linak and Inoguchi (2005) revealed that in 2004, the world production of titanium mineral concentrates had increased to 5.2 million tonnes from 4.6 million tonnes in 2000. Approximately 95 % is used as feedstock for TiO_2 and the remainder is used in titanium metal alloys. In 2004, South Africa (25 %) is the main leading supplier of titanium feedstock followed by Australia (21 %), Canada (14 %), China (8 %), The Ukraine (7%) and Norway (7 %). Approximately 60 plants sites worldwide produce TiO_2 with an average annual capacity of 60000 tonnes. Table 2.1 represents the world TiO_2 capacity by region and process (Linak and Inoguchi, 2005).

Table 2.1: World capacity of TiO_2 (thousand tonnes, gross weight)

Region	1993			1998			2002			2005		
	S	C	Total	S	C	Total	S	C	Total	S	C	Total
North America	202	1288	1488	178	1436	1614	134	1656	1790	80	1717	1797
Central and South America	55	0	55	60	0	60	60	0	60	96	0	96
Western Europe	875	317	1192	913	405	1318	925	472	1397	862	547	1409
Central and eastern Europe	195	0	195	203	0	203	217	0	217	234	0	234
Africa and Middle East	35	50	85	40	80	119	40	100	140	25	100	125
Japan	270	50	319	272	52	324	259	68	327	240	68	308
China	–	–	–	–	–	–	258	408	666	658	15	673
Oceania and other Asia	224	114	338	291	184	475	–	–	–	141	404	545
Total	1856	1819	3672	1957	2157	4113	1893	2704	4597	2336	2857	5187

Where, C: Chloride process

S: Sulfate process

Source: Linak and Inogouchi (2005).

TiO_2 is used in more than 170 countries. The major exporting regions are North America and Australia and most of the countries in the rest of the world are net importers. Table 2.2 shows the world supply and demand for TiO_2 until 2004 (Linak and Inoguchi, 2005).

Table 2.2: World Production and consumption of TiO_2 (thousand tonnes, gross weight)

Region	1997		2001		2004	
	P	C	P	C	P	C
North America						
Canada	75	105	68	90	76	104
Mexico	102	37	124	65	124	64
USA	1340	1129	1340	1100	1511	1162
Central and South America						
Brazil	79	108	78	111	80	124
Other	0	60	0	60	0	85
Western Europe	1113	1099	1150	1100	1254	1183
Central and eastern Europe	136	125	155	155	155	155
Africa and Middle East						
Saudi Arabia	50	10	55	10	90	30
Other Middle East	0	60	0	65	0	120
South Africa	30	25	30	20	20	28
Other Africa	0	15	0	35	0	45
Japan	241	269	257	246	253	238
Oceania and other Asia						
Australia	160	40	181	66	200	40
China	102	170	147	256	350	540
India and Pakistan	50	70	44	77	52	82
Indonesia	–	–	–	–	0	49
Malaysia	–	–	50	28	50	15
Philippines	–	–	–	–	0	33
Republic of Korea	35	100	42	118	40	120
Singapore	–	–	41	16	45	30
Southeast Asia	77	145	–	–	–	–
Taiwan (China)	68	71	123	66	120	66
Thailand	–	–	–	–	0	71
Other	–	–	0	108	0	29
Total	3658	3638	3885	3792	4420	4423

Where, C: Consumption

P: Production

Source: Linak and Inogouchi (2005)

2.1.3 Photoinduced Properties of TiO_2

TiO_2 is an important photocatalytic semiconductor which has some unique properties and its photocatalytic increases remarkable at nanoscale. TiO_2 will produce a pairs of electrons and holes when it absorbs ultraviolet radiation from the sunlight or illuminated source. Marius and Gabriel (2007) claimed that when this situation occurs, the electron valence band of TiO_2 become excited and will promoted the electron to the conduction band of TiO_2. Thus, it will create the negative-electron (e^-) and positive-hole (h^+) pair which called a semiconductor's photo excitation state and at the same time will produce a band gap as shown in Figure 2.7. Therefore, electron-hole pair separation is an important parameter in determining the photocatalytic activity (Cao et al., 1999). Band gap is defined as the energy difference between the valence band and the conduction band. The wavelength of the light necessary for photo-excitation is 1240 (Planck's constant, h)/ 3.2 eV (band gap energy) = 385 nm (Xu et al., 2005).

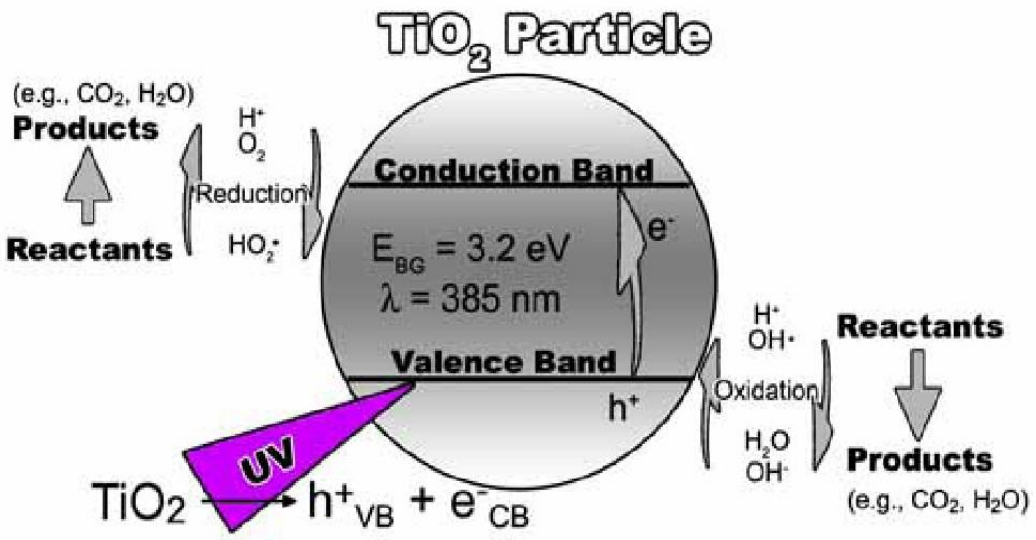

Figure 2.7: Operation of a photochemical excited TiO_2 particle

Source: Marius and Gabriel (2007)

2.1.4 Mechanism of TiO_2

The general equation of a photocatalyzed reaction can be given as shown in equation 2.1.4.1. Where $(Ox)_{ads}$ is the adsorbed oxidant and $(Red)_{ads}$ is the adsorbed reducer.

$$Ox_1)_{ads} + (Red_2)_{ads} \rightarrow Red_1 + Ox_2 \qquad (2.1.4.1)$$

The reaction can be either oxidation or reduction reaction which depends on the sign of Gibbs free energy. According to Hoffman et al., (2005), general mechanism that had been proposed for heterogeneous photocatalysis on TiO_2 is listed below:

(a) Adsorption of Organic Materials:

$Organic \rightleftarrows RX_{ads}$ Where, RX_{ads} represents the organic substrates.

(b) Electron transfer from either the adsorbed substrate (RX_{ads}) or the adsorbed hydroxyl radicals ($^{\cdot}OH_{ads}$) to the holes h^+:

$h^+ + RX_{ads} \rightarrow RX^+_{ads}$

$h^+ + H_2O_{ads} \rightarrow {}^{\cdot}OH_{ads} + H^+$

$h^+ + OH^-_{ads} \rightarrow {}^{\cdot}OH_{ads}$

The second and the third one are the most important steps for the major oxidant, adsorbed hydroxyl radicals ($^{\cdot}OH_{ads}$) which generated in these steps.

(c) Molecular oxygen is presented in oxidative decomposition processes due to its electron acceptor in the electron transfer reaction:

$O_2(g) \rightleftarrows O_{2ads}$

$O_{2ads} \rightarrow 2O_{ads}$

$O_{ads} + e^- \rightarrow O^-_{ads}$

$e^- + O_2 \rightarrow O_2^-$

(d) The superoxide anion can further be involved the following reaction and give more ($^{\cdot}OH_{ads}$) group:

$$H^+ + O_2^- + HO_2 \rightarrow H_2O_2 + O_2$$
$$H_2O_2 + hv \rightarrow 2\,^{\cdot}OH$$

(e) The active free radicals ($^{\cdot}OH_{ads}$) oxidize organic substrate (RX_{ads}) adsorb onto the surface of the semiconductor particles.

$$^{\cdot}OH_{ads} + RX_{ads} \rightarrow \text{Intermediate} \rightarrow \text{Alcohols, Ketones, Acids, } CO_2, H_2O$$

The knowledge of photocatalysis mechanism on TiO_2 surface is not complete yet although some models were proposed. In most of the process, the initial steps involving the reactive oxygen species and organic molecules are particular interest where the oxygen acts as primary electron acceptor and the rate determining process is the electron transfer process. Mao et al., (1991) investigated that hydroxyl radical is the principal reactive oxidant in the photocatalytic reactions of TiO_2. H_2O_2 also can act as an electron acceptor or as a direct source of hydroxyl radicals. Hydroxyl radicals, superoxide, hydrogen peroxide and oxygen can play important roles in photocatalyic reactions which depends on the condition of the reaction involve (Stanford et al., 1993)

Fujishima et al., (2000) stated that photocatalysis is a condition where the excited electrons and holes can be used directly to drive a chemical reaction. The less adjacent coordinate atoms and unsaturated sites of the surface atoms of TiO_2 nanoparticles make it more active than the bulk atoms. Moreover, the surface defects can act as a hole trapping centers in the photocatalysis process. With the decreasing in size, the surface to volume ratio is increases and the surface effect become more active and TiO_2 nanoparticles with a high surface volume ratio can be obtained (Murray et al., 2000).

Wang R et al., (1998) claimed that superhydrophilicity is a newly studied photoinduced property of TiO_2 films. The vacancy of the generated oxygen on the photoexcited TiO_2 surface explained the uniformly spreads of water condition on the

UV light illuminated TiO_2 surface. The van der Waals forces hydrogen bonding interactions between H_2O and ^{-}OH are increase due to the following adsorption of water after generation of oxygen vacancies (Nakajima et al., 2001). The Self-cleaning and anti-fogging of TiO_2 surface can be synthesized according to the superhydrophilic effect. Nakajima et al., (1999) claimed that the superhydrophilic of TiO_2 extraordinary property shows promising applications to the preparation of anti-strain architectural materials, anti-fogging glass and accelerated drying material.

Figure 2.8 shows the schematic representation of superhydrophilicity of TiO_2. In Figure 2.8(a), the electrons in the conduction band have the affinity to reduce TiO_2 to form an intermediate species. In the following steps in Figure 2.8(b), the holes in the valence band push away the oxygen atoms and create vacant sites which can be easily created if there are some surface defects. Lastly, in Figure 2.8(c), The TiO_2 with the vacant sites can dissociate water into H and OH groups which leads to superhydrophilicity.

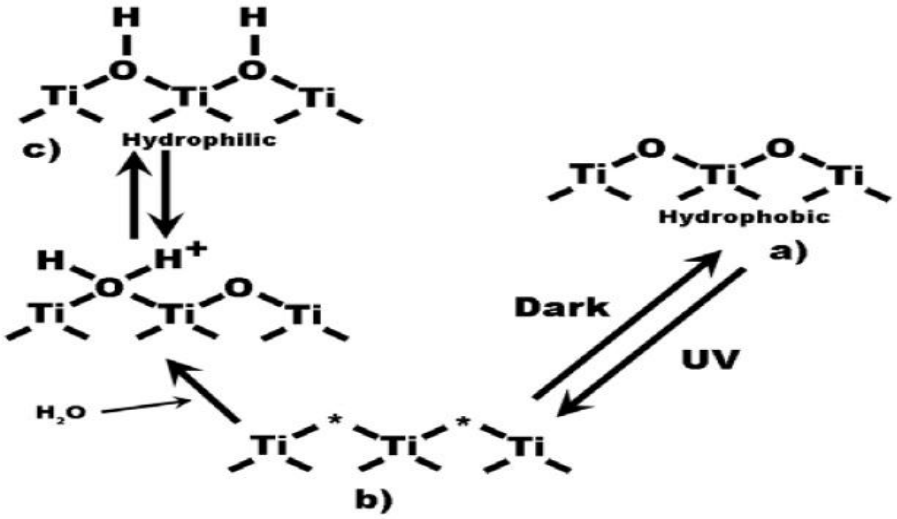

Figure 2.8: Superhydrophilicity of TiO_2 (a) Hydrophobic TiO_2 (b) TiO_2 with vacant sites (c) hydrophilic TiO_2

Source: Alp (2009)

Nishimura et al., (2010) revealed that numerous organic materials can be mineralized into carbon dioxide and water under UV radiation on TiO_2 nanoparticles suspension. The preparation of particles suspension with a high degree of homogeneousness and stability in the aqueous phase is the main key parameter which affecting the photocatalytic reactions. The way to improve the feasibility of organic substance removal is by increasing the stability suspension and the adsorption of various organic molecules onto TiO_2 nanoparticles surface sites (Xu et al., 2003).

Miyauchi et al., (2004) stated that in aqueous systems, nanoparticles of TiO_2 always carry charge due to the ionization, the adsorption ions or the preferential substitution of ions from the particles surfaces. The physical properties of TiO_2 nanoparticles suspensions are mainly dependent on the behaviour of aqueous suspensions. It is especially reactive to the electrical and ionic structure if the particle is in a liquid surface. Zeta potential is used to identify the intensity of repulsive forces among particles and the stability of dispersion. According to Molino et al., (1999), this parameter is the key on the stability control of TiO_2 nanoparticles in suspension and the adsorption properties of TiO_2 nanoparticles sites.

Besides that, Mandzy et al., (2005) stated that some studies showed the isoelectric points (IEP) could be correlated with the photocatalytic activity of TiO_2 particles and the surface charge of TiO_2 particles affected the inactivation kinetics of bacteria considerably. Samples with different chemical compositions had all different zeta potential dependence on pH values of particles (Gumy et al., 2006). Figure 2.9 shows the application of TiO_2 as photocataysts in photoreduction process where it helps to convert CO_2 into a reusable hydrocarbon

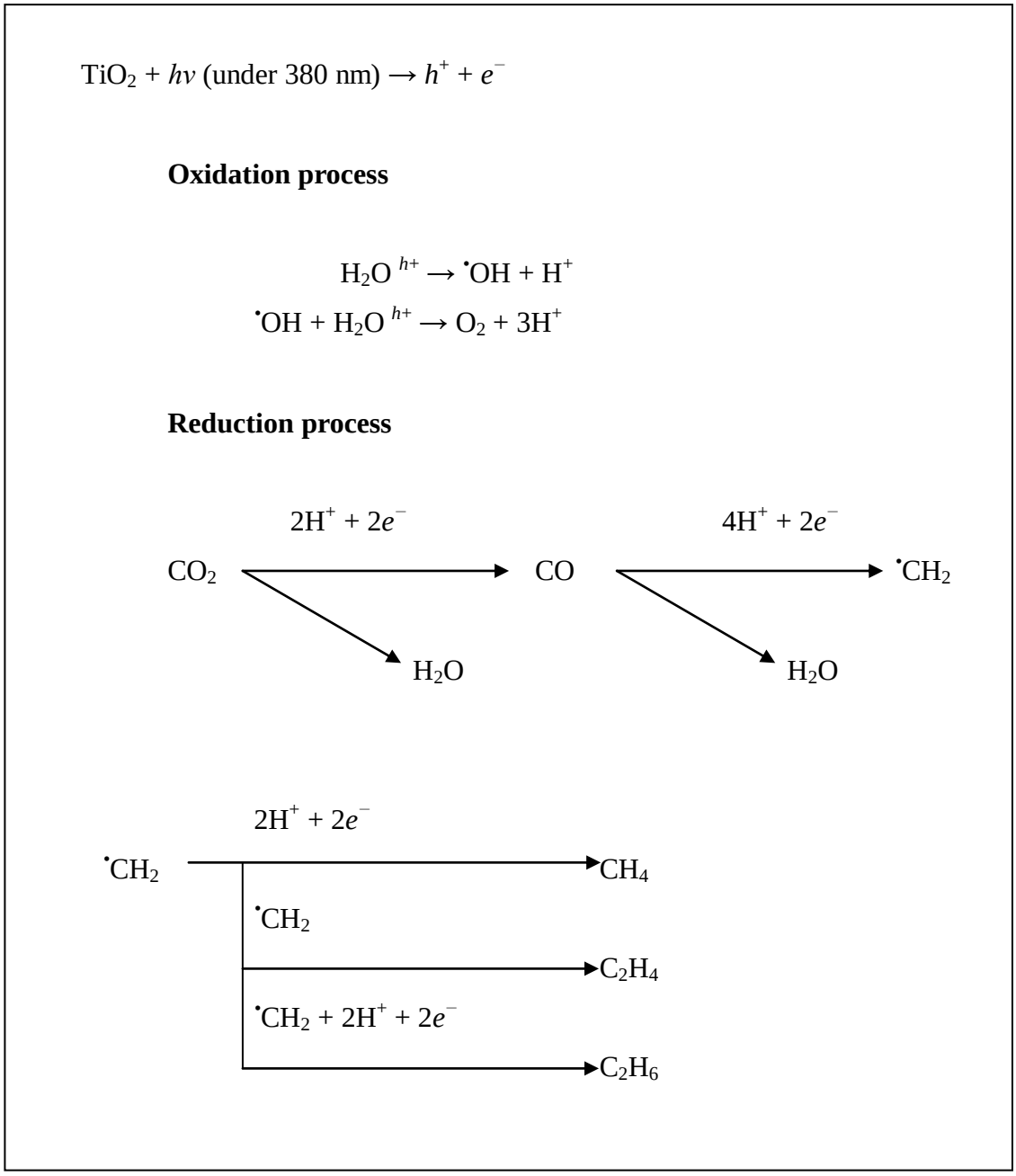

Figure 2.9: Mechanism of photoreduction process

Source: Nishimura et al., (2010)

2.2 Aluminium Oxide (Al_2O_3)

Oberlander (1984) was defined alumina (Al_2O_3) as a white powder that normally produced from bauxite ores. It is one of the most widely used advanced ceramic materials with applications ranges from spark plugs to catalyst materials. Al_2O_3 attractive for engineering applications due to its chemical and thermal stability, relatively good strength and electrical insulation characteristic combined with availability in abundance have made. Other than that, it is also a relatively low cost material, and by using a number of fabrication methods, it can easily be formed and finished. Al_2O_3 has several allotropic forms, but only the usual type or α-alumina is considered. It has an internal crystal structure where the oxygen ions are packed in a closed packed hexagonal (cph) arrangement with aluminium ions in two-thirds of the octahedral sites.

According to Oberlander (1984), there are 27 aluminum chemicals listed as Al_2O_3 which show a wide range of physical and chemical properties of Al_2O_3 in a research conducted by McZura et al. (1978). There are varieties of physical properties of synthetic commercial aluminas which are suitable to be use as adsorbents and catalysts. Aluminas that have a specific area from 0.01 m^2/g to 400 m^2/g, volume of the pores from 0.1 cm^3/g to 1.4 cm^3/g and average pore size from 2nm or 20Å to 177μm are known as “active aluminas” (Pedro et., al 2000).

Oberlander (1984) also revealed that “active alumina” is commonly used in catalyst technology typically means for aluminas that have high surface areas and considerable chemical activities. It also used as a term patented by ALCOA (ALCOA 1969, Goodboy and Downing 1990) which referred to aluminas that exhibit an ability in adsorbing significant quantities of water from gases and liquids. Other than that active aluminas also used in advanced ceramics which is used as a contraction of the term “reactive alumina” (ALCOA, 1972). The reactive aluminas are referring to aluminas which, after pressed without the addition of sintering catalysts and fired at high temperatures which smaller than melting point of Al_2O_3, they will sinter into very hard low-porosity pieces having α-alumina structure.